

U.S. Department of Agriculture Agricultural Research Service Mahantango Creek Watershed, Pennsylvania, United States: Long-term water quality database

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[1] A long-term water quality database has been developed by the U.S. Department of Agriculture (USDA) Agricultural Research Service (ARS) Pasture Systems and Watershed Management Research Unit to support water quality research within WE-38, a 7.3 km² experimental subwatershed of Mahantango Creek Watershed located in east central Pennsylvania and draining to the Susquehanna River. Water quality data were collected at the outflow of WE-38, with record lengths of 24 years (1983–2007) for nitrate-N and ammonium-N and 23 years (1984–2007) for orthophosphate-P. Data are available on USDA ARS Sustaining the Earth's Watersheds—Agricultural Research Data System (STEWARDS) Web site.

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1. Introduction

[2] Measuring long-term water quality is necessary for studying the effects of changing land uses and climate variability and to show improvements in water quality with the adoption of conservation practices. Since 1983, the U.S. Department of Agriculture (USDA) Agricultural Research Service (ARS) Pasture Systems and Watershed Management Research Unit (PSWMRU) has conducted water quality monitoring in the 7.3 km² experimental subwatershed of the Mahantango Creek Watershed that is designated WE-38. The goal of this monitoring is to support long-term intensive research on the impacts of agriculture on water quality in the northeastern United States [Bryant *et al.*, 2011]. Located about 48 km north of Harrisburg, Pennsylvania, in the Northern Appalachian Ridges and Valleys Province, the WE-38 watershed drains rolling farmland in the northern part of the 420 km² Mahantango Creek Watershed, a tributary of the Susquehanna River [Bryant *et al.*, 2011, Figure 1]. This paper provides a history of water quality data collection and analytical techniques employed in WE-38 and describes the water quality data set that is a component of the Sustaining the Earth's Watersheds—Agricultural Research

Data System (STEWARDS), a digital repository for long-term watershed monitoring data [Sadler *et al.*, 2008].

2. Sample Site and Collection Methods

[3] The water quality sampling site is located 130 m upstream from the WE-38 weir (40°42'16"N, 76°35'16"W) and 30 m upstream of a footbridge that spans the stream channel (Figure 1). At base flow (discharge ~0.16 m³ s⁻¹), the width of the stream channel is about 1.8 m, and the thalweg depth is about 0.2 m.

[4] A technician visits the site three times per week, usually on Mondays, Wednesdays, and Fridays. During each site visit, a single grab sample is collected in a 473 mL high-density polyethylene (HDPE) bottle from just below the water surface at the channel thalweg (approximately in the center of the channel). Stream temperature (°C) is measured at the time of sampling using an alcohol thermometer. Field blanks are occasionally collected for specific studies but are not part of the long-term database.

[5] Following field visits, samples are stored in ice-filled coolers and immediately transported to the field station in Klingerstown, Pennsylvania, for further processing and analysis. A 50 mL sample aliquot is filtered through a 0.45 μm filter and transferred to a centrifuge tube. A VWR Traceable Expanded Range Conductivity Meter and a Thermo Scientific Orion 2 Star Benchtop pH Meter are used to measure the electrical conductivity and the pH of the unfiltered samples. Filtered and unfiltered samples are then packed on ice in large coolers, shipped immediately to the water quality laboratory in University Park, Pennsylvania, and stored at 4°C in the

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Figure 1. Photograph of the WE-38 water quality sampling site, 30 m upstream from the bridge and 130 m upstream from the compound weir, which is located at 40°42'16"N, 76°35'16"W.

dark until they are analyzed for nutrients and other chemical constituents.

3. Analytical Techniques

[6] Various analytical techniques have been employed over the 24 year data period, reflecting changes in technology (e.g., increases in sensitivity, changing to an automated methodology), reduction of hazardous material generation, or the needs of researchers working at the site. Blank and replicate samples were run with each batch of samples in the lab as a matter of course, and at the time of switching methods, duplicates of all samples were analyzed to ensure data continuity within the laboratory; unfortunately, those data were not retained. An examination of the data, however, reveals no sudden increase or decrease in concentration reported at the times of switching methods, one indication that the data is internally consistent. The following subsections summarize the analytical techniques used to determine concentrations for nitrate-N, ammonium-N, and orthophosphate-P, the dates on which these techniques were used, and the sensitivities of each method. In all cases, samples that were above the range indicated were diluted and reanalyzed.

3.1. Nitrate-N

[7] From 3 January 1983 to 12 August 1986, nitrate-N concentrations were determined following EPA standard method 353.2 [U.S. Environmental Protection Agency (EPA), 1983], with a sensitivity range of 0.05–10 mg N/L. From 21 August 1986 to 30 June 1997, nitrate-N concentrations were determined by ion chromatography using a Wescan 269-013 anion column (Wescan Instruments, Santa Clara, California) and KHP eluent, with a sensitivity range of 0.05–10 mg N/L. From 2 July 1997 to 31 December 2007, nitrate-N was determined using a Lachat Quick Chem 8000 following the Lachat Quick Chem method 10-107-04-1-A (Lachat Instruments, Quick Chem method 10-107-04-1-A: Nitrate/nitrite, nitrite in surface water, wastewater,

Milwaukee, Wisconsin, 1995), with a sensitivity range of 0.2–20.0 mg N/L.

3.2. Ammonium-N

[8] From 2 February 1983 to 10 December 1990, ammonium-N concentrations were determined using a cartridge produced by Bran and Luebbe (now SEAL Analytical, Hamburg, Germany) following EPA standard method 350.1 [EPA, 1993], with a sensitivity range of 0.01–2.0 mg N/L. From 12 December 1990 to 30 June 1997, ammonium-N was determined using a MultiTest cartridge from Bran and Luebbe (now SEAL Analytical, Hamburg, Germany) following Bran and Luebbe method 696-82W (Bran and Luebbe, Method 696-82W for the Technicon Autoanalyzer II, Buffalo Grove, Illinois, 1989), with a sensitivity range of 0.02–3 mg N/L. From 2 July 1997 to 31 December 2007, ammonium-N was determined using a Lachat Quick Chem 8000 following Lachat Quick Chem method 10-107-06-1-B (Lachat Instruments, Quick Chem method 10-107-06-1-B: Determination of ammonia (phenolate) by flow injection analysis, Milwaukee, Wisconsin, 2001), with a sensitivity range of 0.01–1.0 mg N/L.

3.3. Orthophosphate-P

[9] From 4 April 1984 to 7 January 1985, orthophosphate-P concentrations were determined following EPA standard method 365.2 [EPA, 1971], with a sensitivity range from 0.01 to 0.5 mg P/L. From 14 February 1985 to 17 March 1987, orthophosphate-P concentrations were determined using the Technicon Industrial method 155-71W (Technicon Industrial Systems, Industrial method number 155-71W: Orthophosphate in water and seawater, Tarrytown, New York, 1973), following EPA standard method 365.2 [EPA, 1971] using a AAI cartridge from Bran and Luebbe (now SEAL Analytical, Hamburg, Germany), with a sensitivity range of 4.0–124.0 $\mu\text{g P/L}$. From 24 March 1987 to 30 June 1997, orthophosphate-P concentrations were determined as per EPA standard method 365.2 [EPA, 1971]

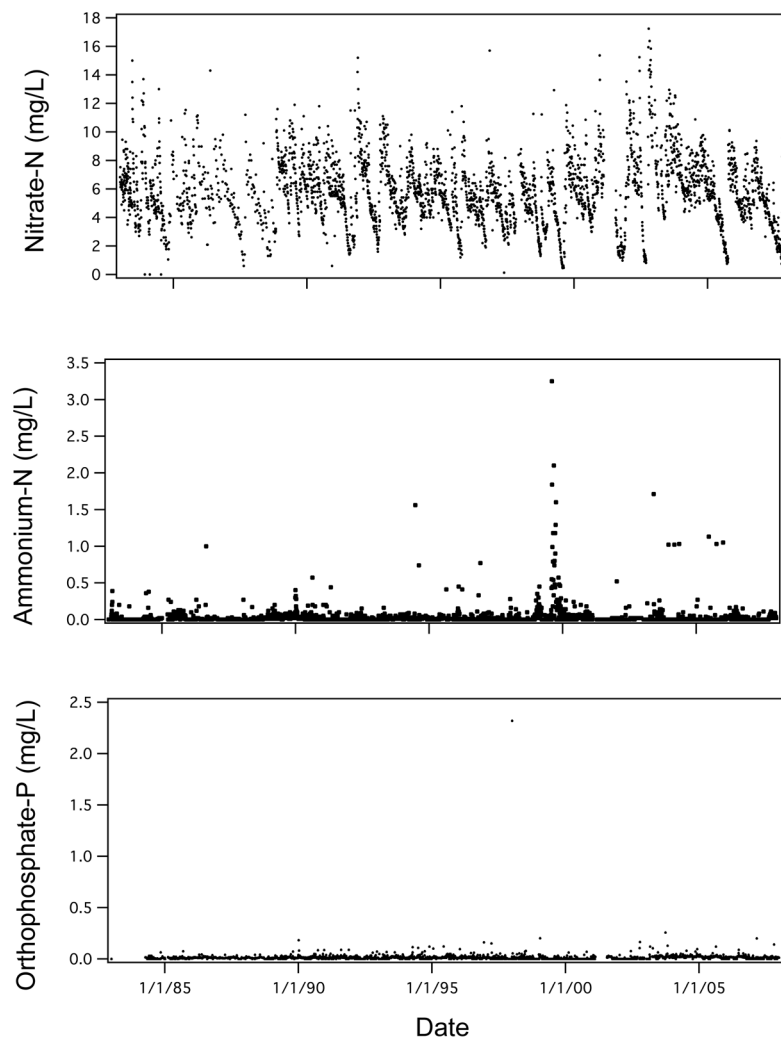


Figure 2. (top) Nitrate-N, (middle) ammonium-N, and (bottom) orthophosphate-P concentrations in WE-38 streamflow for the period of record (1983–2007).

using a Milton Roy Spectronic 1001 spectrophotometer (Milton Roy Co., Ivyland, Pennsylvania), with a sensitivity range of 0.01–0.5 mg P/L. From 2 July 1997 to 31 December 2007, orthophosphate-P was determined using a Lachat Quick Chem 8000 following Lachat Quick Chem method 10-115-01-1-T (Lachat Instruments, Quick Chem method 10-115-01-1-T: Determination of orthophosphate in waters by flow injection analysis colorimetry, Milwaukee, Wisconsin, 1996), with a sensitivity range of 0.005–2.50 mg P/L.

4. Frequency of Sampling and Length of Water Quality Record

[10] As mentioned in section 2, samples are typically collected three times per week. Sampling is conducted irrespective of hydrologic events, though for some intensive studies there have been as many as 22 samples per month for short periods. For the entirety of the 24 year record, there are few significant gaps in the water quality data, though some gaps in excess of 1 month do exist. In general, 96%

of the entire record exists for nitrate-N and 95% exists for ammonium-N and orthophosphate-P.

5. General Description of Water Quality

[11] A graphical representation of all data (Figure 2) shows patterns of nitrate-N, ammonium-N, and orthophosphate-P for the period of record. Nitrate-N concentrations range from nondetect to 17.2 mg N/L, while ammonium-N concentrations range from nondetect to 3.3 mg N/L. Orthophosphate-P concentrations range from nondetect to 2.5 mg P/L and are typically low (<0.3 mg P/L). Monthly mean values averaged over the entire period of record are plotted to illustrate seasonal variations in nitrate-N, ammonium-N, and orthophosphate-P (Figure 3).

6. Examples of Data Use

[12] Since 1983, when water quality monitoring began in WE-38, a number of water quality research studies have been conducted using the data presented here as well as additional water quality constituents that were measured on

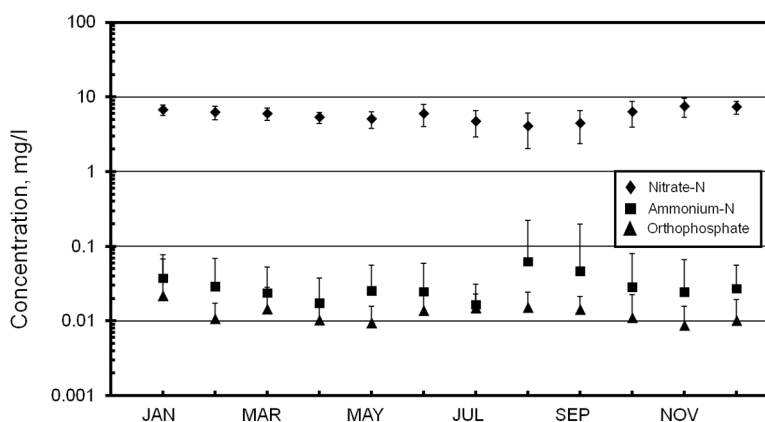


Figure 3. Monthly mean concentrations of nitrate-N, ammonium-N, and orthophosphate-P concentrations in WE-38, with error bars indicating one standard deviation from the mean.

a study-specific basis. Initially, researchers used relative chemical signatures of nitrate-N, ammonium-N, sulfate, chloride, orthophosphate-P, and total phosphorus in seepage, surface runoff, stormflow, base flow, and runoff to examine hydrology of the near-stream zone [Pionke *et al.*, 1988; Schnabel *et al.*, 1993]. They found that, during a storm event, inputs to the stream begin with dilution of stream concentrations from direct rainfall. This is followed by a rapid saturation and increase in the area of the seep zone near the stream, resulting in inputs to the stream being largely dominated by surface runoff with little effect to the regional water table. Stream inputs transition from surface to largely subsurface flow as the regional groundwater table rises in response to the storm.

[13] As nutrient losses from agricultural operations became more of a concern, research focus changed to quantifying and managing nutrient export from WE-38. Researchers [Pionke and Kunishi, 1992] examined various fractions of orthophosphate-P in storm and base flows and found that, contrary to conventional wisdom, which suggests that erosion control strategies would limit phosphorus loss from agricultural lands, up to 50% of algal available phosphorus (the sodium hydroxide extractable fraction) and 30% of total phosphorus exported from the watershed were in soluble forms. A further examination of nutrient transport during storm and base flows [Pionke *et al.*, 1996, 1999, 2000] and definition of hydrological source areas [Gburek and Folmar, 1999] found that 66%–70% of the water soluble phosphorus was exported during the 10% of time defined as stormflow and that 66% of total export of phosphorus occurred in winter and spring. Conversely, most of the nitrate-N export (60%) occurred during nonstorm periods, also in winter and spring, and arose from higher concentrations in base flows. Furthermore, long-term nitrate-N export from the watershed corresponded with the nitrogen excess computed by a nitrogen balance obtained through farmer surveys [Pionke *et al.*, 2000]. This research strongly suggests that the greatest opportunity for controlling export of soluble phosphorus is in controlling the hydrologically active phosphorus source areas and needs to be storm-based (for example, focusing on areas in the near-stream seep zone), while nitrogen management and control

decisions should be based on balancing nitrogen use over the entire area of the watershed.

7. Data Availability

[14] Long-term water quality data available from the outlet of the WE-38 watershed include data on nitrate-N (January 1983–December 2007), ammonium-N (February 1983–December 2007), and orthophosphate-P (April 1984–December 2007). Water quality data are presented in their raw form, without assumptions or edits. These data are publicly available on the USDA ARS Sustaining the Earth's Watersheds—Agricultural Research Data System (STEWARDS) Web site (<http://www.ars.usda.gov/Research/docs.htm?docid=18622>). Other water quality data, including pH, electrical conductivity, water temperature, and cation data, which exist sporadically for the period of record and for dates beyond 31 December 2007, are maintained in-house. Information on accessing these data and relevant links are available at <http://www.ars.usda.gov/Services/docs.htm?docid=21452>.

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